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Electronic Supplementary Information

Cobalt-Catalyzed Enantioselective Radical Hydroamination of Alkenes with N-Fluorobenzenesulfonimides: Theoretical Insight of Enantio-Determining S_N2-like Reductive Elimination

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Table of Contents

COMPUTATIONAL DETAILS S1
REFERENCES S9

COMPUTATIONAL DETAILS

1. Correction of Translational Entropy in Solution

We evaluated the electronic energy (E_{sol}) with zero-point energy correction in solution. For each species, the E_{sol} is defined through equation (S1):

$$E_{\mathrm{sol}} = E_{sol}^{pot} + E_{gas}^{v_0} \tag{S1}$$

the E_{sol}^{pot} is the potential energy including non-electrostatic energy in solution and $E_{gas}^{v_0}$ delegates the zero-point vibrational energy in the gas phase. In a bimolecular process, such as the interaction between Co(II) complex and NFSI, the entropy change which can decreases considerably must be taken into consideration. In such case, Gibbs energy (G_{sol}^{o}) need be computed as follows:

$$\begin{aligned} G_{sol}^{o} &= H_0 - T(S_{\mathrm{r}}^{o} + S_{\mathrm{v}}^{o} + S_{\mathrm{t}}^{o}) \\ &= E^{T} + P\Delta V - T(S_{\mathrm{r}}^{o} + S_{\mathrm{v}}^{o} + S_{\mathrm{t}}^{o}) \\ &= E_{sol} + E_{therm} - T(S_{\mathrm{r}}^{o} + S_{\mathrm{v}}^{o} + S_{\mathrm{t}}^{o}) \end{aligned} \tag{S2}$$

where ΔV is 0 in solution, E_{therm} is the thermal correction by translational, vibrational, and rotational movements, and S_{r}^{o}, S_{v}^{o}, and S_{t}^{o} are rotational, vibrational, and translational entropies, respectively. In general, the Sackur-Tetrode equation is used to evaluate translational entropy S_{t}^{o}. In solution, however, the usual Sackur-Tetrode equation cannot be directly applied to the evaluation of S_{t}^{o}, because the translation movement is suppressed very much in solution.[S1] In this context, the translational entropy was corrected with the method developed by Whitesides et al., where the rotational entropy was evaluated in a normal manner. Thermal correction and entropy contributions of vibration movements to the Gibbs energy were evaluated with the frequencies calculated at 298.15 K and 1 atm.

2. Activation barrier of single electron transfer step

According to the Marcus equation, the reorganization energy λ is normally decomposed into internal energy (λ_i) and external energy (λ_o). The internal reorganization energy λ_i can be estimated according to the equation (S3):

$$\lambda_i = [E^D(Q_R) + E^A(Q_R)] - [E^D(Q_P) + E^A(Q_P)] \tag{S3}$$

where Q_R and Q_P are the equilibrium geometries of the reactants and products, respectively. In addition, the external reorganization energy λ_o may be calculated from equation (S4−S6):

$$\lambda_o = (332\ \mathrm{kcal/mol})(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{\mathrm{R}})(\frac{1}{\varepsilon_{op}} - \frac{1}{\varepsilon}) \tag{S4}$$

$$\lambda = \lambda_o + \lambda_i \tag{S5}$$

$$\Delta G^{\circ\neq} = \frac{(\Delta G_\mathrm{r} + \lambda)^2}{4\lambda} \tag{S6}$$

where a_1 is the radii of the oxidant, a_2 is the radii of the reductant, $R = a_1 + a_2$, $\varepsilon\varepsilon_{op}$ is the optical dielectric constant (ε_{op} = 2.25), ε is the static dielectric constant for the tetrahydrofuran solvent (ε= 7.425), and ΔG_r is the free energy change of the reaction.

Table S1 Relative energies of selected species involving different spin states calculated with using various functionals and basis sets.

Functionals	**^{4}N1**	**^{2}N1**	**^{6}N4**	**^{4}N4**	**^{2}N4**	**^{2}N7**	**^{4}N7**	**^{6}N7**	**$^{U\text{-}2}$N9a**	**$^{U\text{-}4}$N9a**	**^{2}N10a**	**^{4}N10a**
[a]**M06**	0.0	10.1	0.0	1.4	10.5	0.0	4.1	15.1	0.0	3.5	0.0	3.5
[b]**M06**	0.0	4.8	0.0	7.7	8.4	0.0	13.6	27.9	0.0	2.8	0.0	3.2
[c]**Sol-M06**	0.0	11.6	0.0	4.8	10.3	0.0	2.3	13.5	0.0	0.8	0.0	2.8
[d]**M062X**	0.0	17.0	0.0	39.0	45.4	0.0	11.2	13.7	0.0	0.5	0.0	4.7
[e]**B3-D3**	0.0	1.4	0.0	1.0	4.2	0.0	16.7	27.5	0.0	2.4	0.0	6.9
[f]**TPSSH**	0.0	-12.8	0.0	1.3	-18.8	0.0	23.6	37.4	0.0	18.5	0.0	23.6

[a] at the SMD(THF)/(U)M06/[6-311++G(d,p)/SDD(Co)]//(U)M06/[6-31G(d)/LanL2DZ(Co)] level

[b] at the SMD(THF)/(U)M06/[def2-TZVPP]//(U)M06/[def2-SVP] level

[c] at the SMD(THF)/(U)M06/[6-311++G(d,p)/SDD(Co)]//SMD(THF)/(U)M06/[6-31G(d)/ LanL2DZ(Co)] level

[d] at the SMD(THF)/(U)M062X/[6-311++G(d,p)/SDD(Co)]//(U)M062X/[6-31G(d)/LanL2DZ(Co)] level

[e] at the SMD(THF)/(U)B3-D3/[6-311++G(d,p)/SDD(Co)]//(U)B3-D3/[6-31G(d)/LanL2DZ(Co)] level

[f] at the SMD(THF)/(U)TPSSH/[def2TZVP]//(U)M06/[6-31G(d)/LanL2DZ(Co)] level

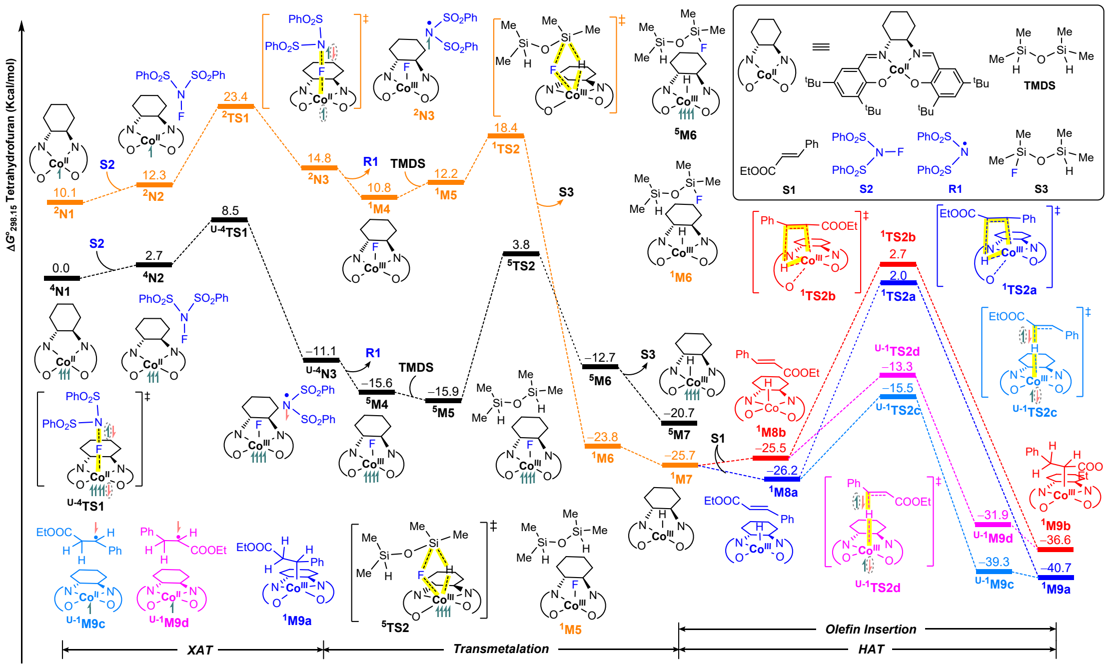

Fig. S1 Gibbs energy profiles ($\Delta G^\circ_{298.15}$) of benzenesulfonimide radical dissociation from $^{U\text{-}4}$**N3** followed by transmetalation and HAT.

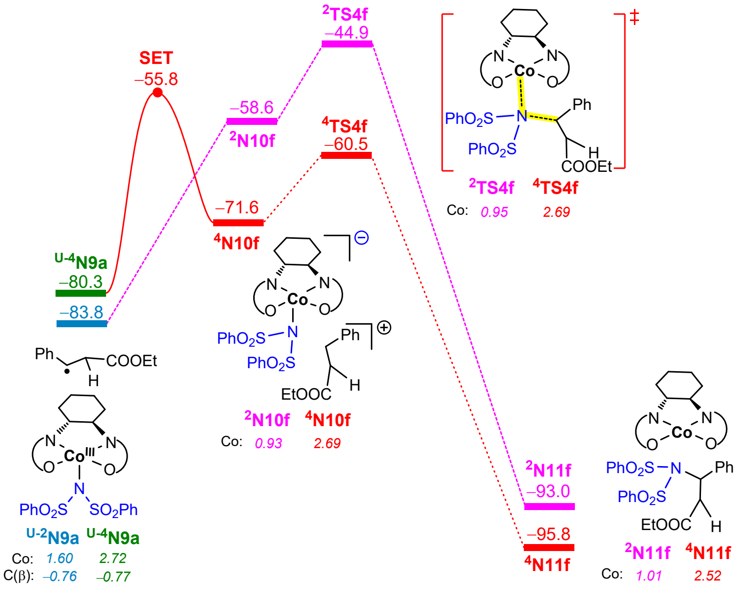

Fig. S2 Gibbs energy profiles ($\Delta G^\circ_{298.15}$) of carbon cation electrophilic attack pathway.

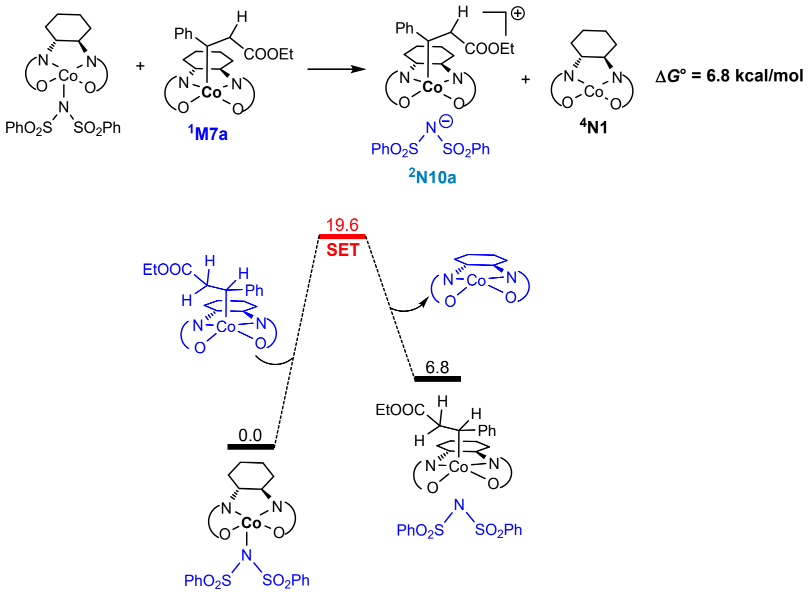

Fig. S3 Thermodynamic and kinetic evaluation for the oxidation of Co^{III}-alkyl by Co^{III}-N(SO$_2$Ph)$_2$ to arrive at the Co^{IV}-alkyl intermediate.

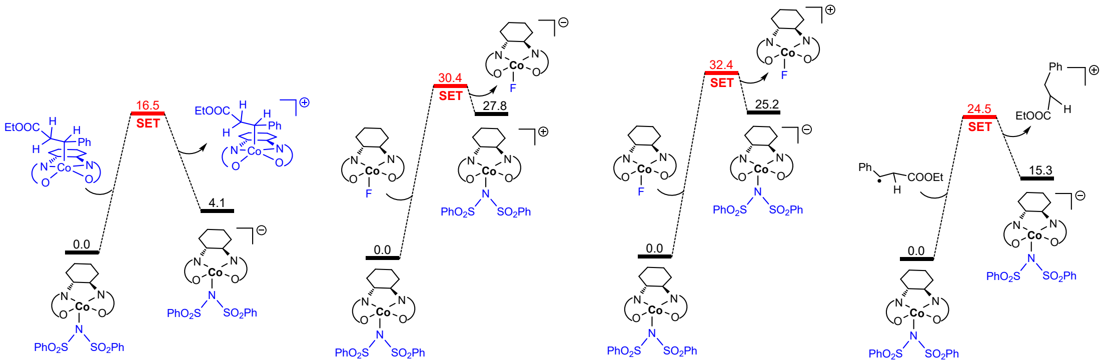

Fig. S4 Kinetic energy barrier calculations for steps involving SET.

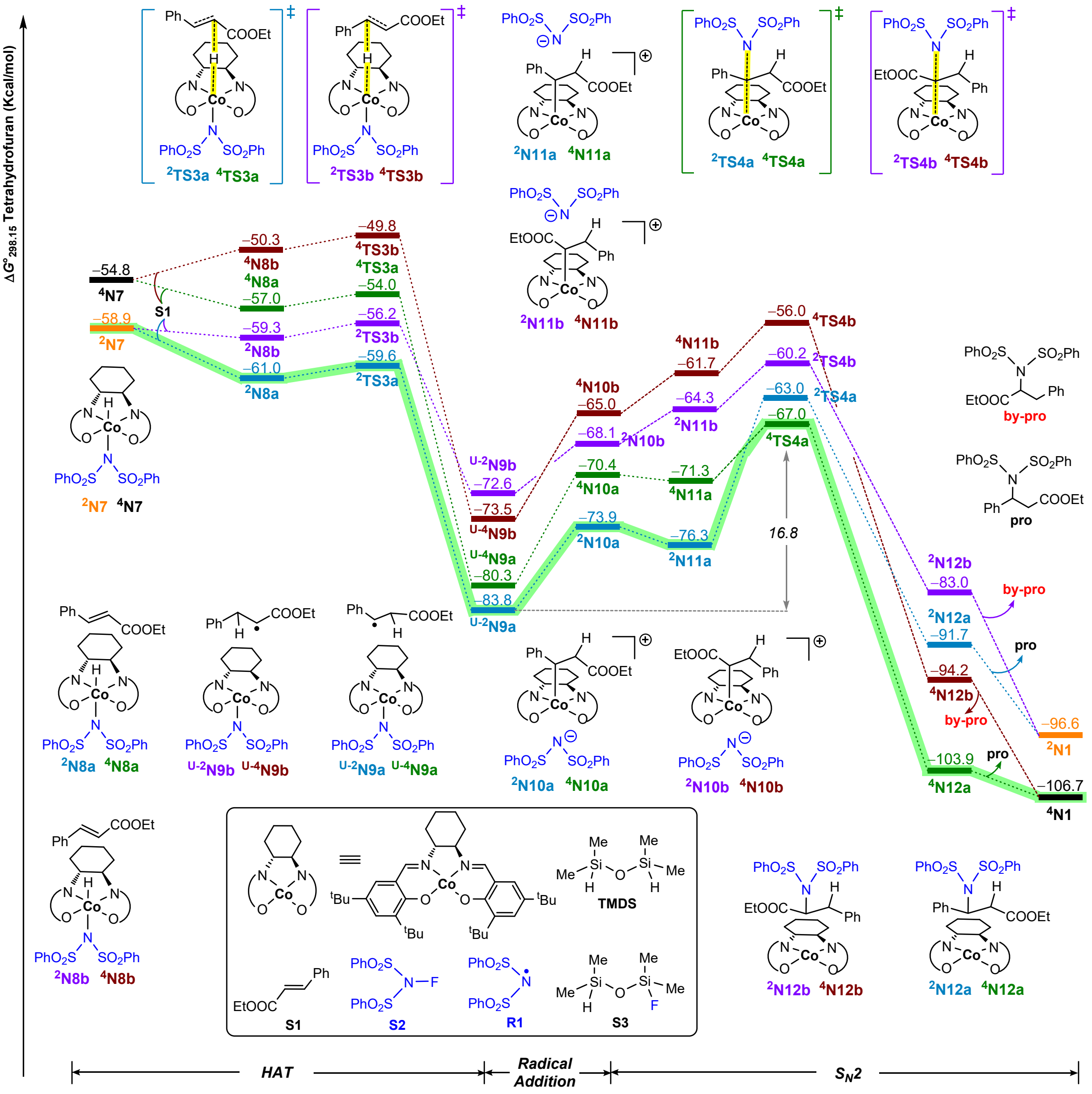

Fig. S5 Gibbs energy profiles ($\Delta G^{\circ}_{298.15}$) of cobalt catalytic cycle.

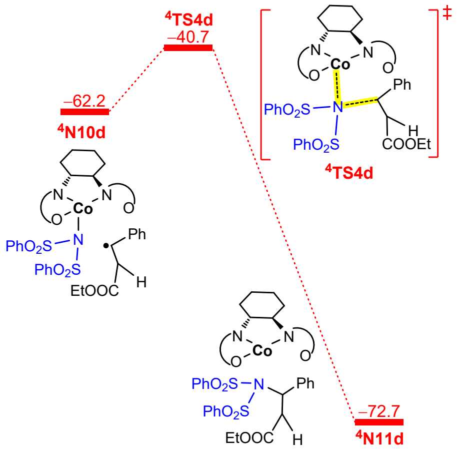

Fig. S6 Gibbs energy profiles ($\Delta G^{\circ}_{298.15}$) of benzylic radical attacking the $N(SO_2Ph)_2$ pathway with one ligand's oxygen atom changed to the axial position.

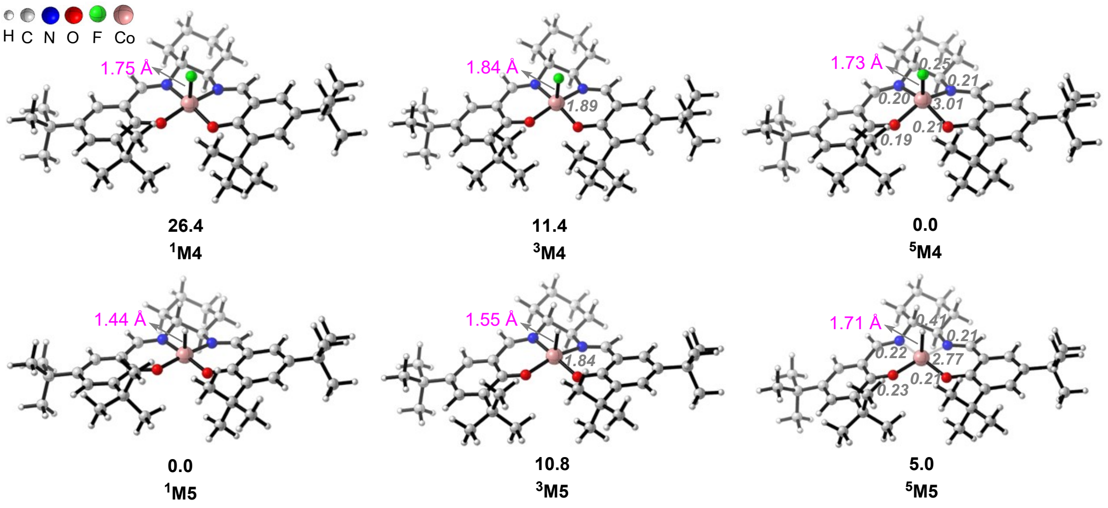

Fig. S7 Comparison of optimized geometries of L1*Co^{III}F and L1*Co^{III}H compounds with different electron spin states.

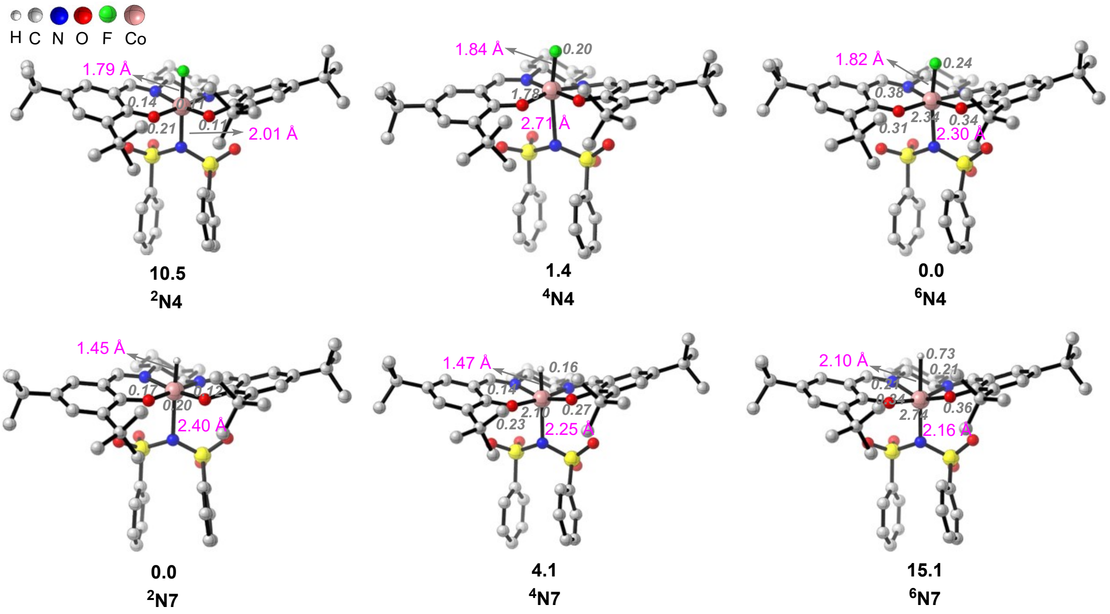

Fig. S8 Comparison of optimized geometries of L1*Co^{IV}F and L1*Co^{IV}H compounds with different electron spin states.

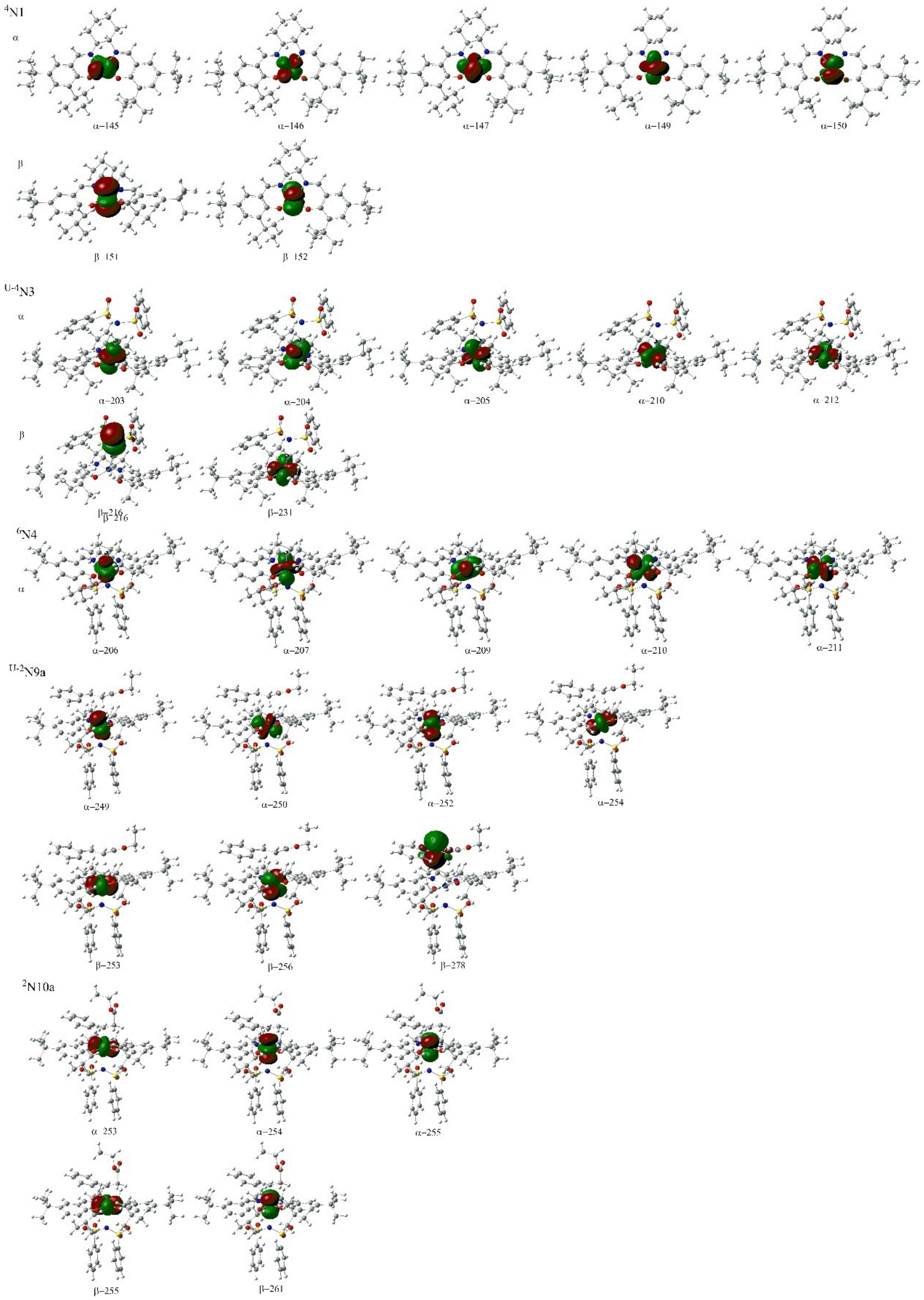

Fig. S9 Selected d orbitals of cobalt compounds in various valence states (**^{4}N1**, **$^{U-4}$N3**, **^{6}N4**, **$^{U-2}$N9a**, **^{2}N10a**).

From the NBO analysis:

(i) The cobalt compound **^{4}N1** has five α electrons and two β electrons, indicating it is a divalent cobalt compound in a quadruple state.

(ii) The cobalt compound **$^{\text{U-4}}$N3** has five α electrons and one β electron, along with a β fluorine atom radical, also suggesting it is a divalent cobalt compound in a quadruple state.

(iii) The d orbital of **^{6}N4** contains five α electrons, indicating that **^{6}N4** is a tetravalent cobalt compound in a sextet state.

(iv) The cobalt compound **$^{\text{U-2}}$N9a** has four α electrons and two β electrons, along with a β benzylic carbon radical, classifying it as a divalent cobalt compound in a quadruple state.

(v) The d orbital of **^{2}N10a** has three α electrons and two β electrons, indicating that **^{2}N10a** is a tetravalent cobalt compound in a doublet state.

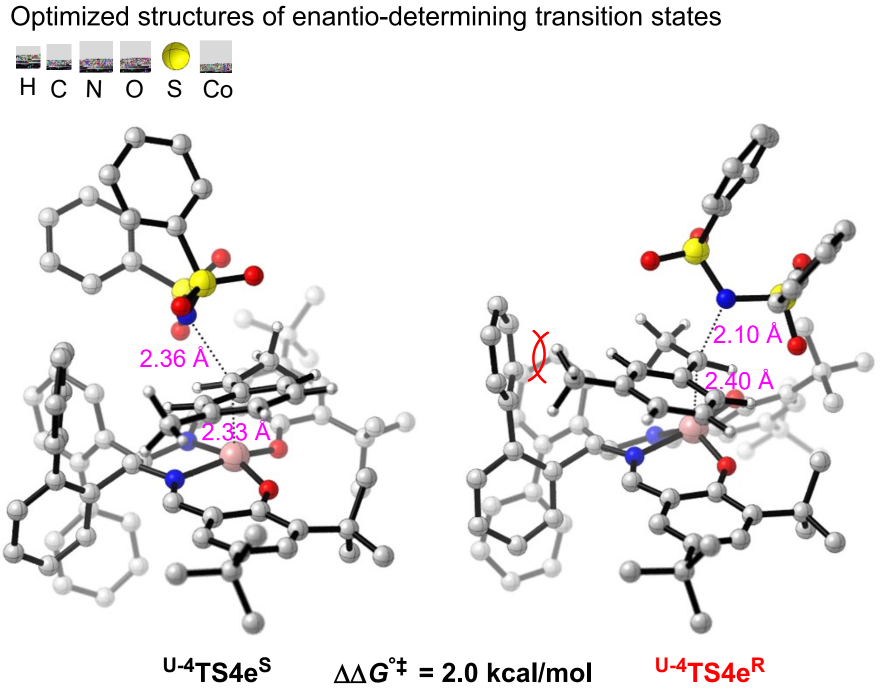

Fig. S10 Comparison of optimized geometries of enantio-determining transition states **$^{\text{U-4}}$TS4e$^{\text{S}}$** and **$^{\text{U-4}}$TS4e$^{\text{R}}$**.

REFERENCES

S1. (a) Sakaki, S.; Ohnishi, Y. Y.; Sato, H., Theoretical and Computational Studies of Organometallic Reactions: Successful or Not? *Chem. Rec.* **2010**, *10*, 29–45; (b) Ishikawa, A., Nakao, Y., Sato, H.; Sakaki, S., Oxygen Atom Transfer Reactions of Iridium and Osmium Complexes: Theoretical Study of Characteristic Features and Significantly Large Differences between These Two Complexes. *Inorg. Chem.* **2009**, *48*, 8154–8163; (c) Ishikawa, A., Nakao, Y., Sato, H.; Sakaki, S., Pd(II)-Promoted Direct Cross-Coupling Reaction of Arenes via Highly Regioselective Aromatic C–H Activation: A Theoretical Study. *Dalton Trans.* **2010**, *39*, 3279–3289.